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Promotive Effect of Hydrogen Sulfide on the Activities of Various Solid Catalysts

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Abstract

For acid catalyzed reactions, the catalytic activities of metal ion exchanged Y zeolites (MeY, Me=Cd²⁺, Cu²⁺, Ni²⁺, Co²⁺, Ag⁺ and Zn²⁺), and metal ion supported on silica-alumina, silica gel and alumina (Me-SiO₂-Al₂O₃, Me-SiO₂ and Me-Al₂O₃, Me=Ag⁺, Cu²⁺, Cd²⁺, Co²⁺ and Ni²⁺) were enhanced by the treatment with H₂S.

From the infrared spectroscopic study, it was concluded that an increase in catalytic activity of catalysts by H₂S treatment was attributed to the formation of new Brönsted acid sites on the catalyst surface. These catalysts contained metal ions which bind strongly to H₂S. Thus, it was concluded that an increase in catalytic activity was strongly dependent on the affinity of metal ions in catalysts toward H₂S.

1. Introduction

Recently, it has been reported¹⁻⁹⁾ that sulfur compounds such as H₂S and SO₂ adsorbed on catalyst surface promote the catalytic activities of solid catalysts. However, hardly any reports concerning the mechanism of the promoting action of these adsorbed sulfur compounds on the catalytic activity and the interaction between sulfur compounds and catalyst surface have been published.

In the present paper, we have systematically studied the effect of H₂S treatment on the catalytic activities of various solid catalysts and the adsorption states of H₂S on catalyst surface to obtain more accurate knowledge regarding the interaction between H₂S and solid catalyst surface.

2. Experiment

2.1 Experimental Apparatus and Procedure

To examine the activity of catalysts for various acid catalyzed reactions, a conventional pulse reactor connected to a Yanagimoto GCG-550T gaschromatograph and a conventional continuous flow reactor were used. In the pulse reaction, 2μl of the reactants were injected into the reactor by passing a carrier gas with a micro-syringe. In a continuous flow reaction, the reactants were continuously supplied to the catalyst bed with the micro-feeder and the products were collected with an ice trap. Helium, dried with a molecular sieve, was used as

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the carrier gas. The reactor was a U-type pyrex glass tube which was heated with an electric furnace. The temperature of the catalyst bed was controlled within $\pm 1^\circ\text{C}$.

H₂S treatment of the catalysts were carried out by injection of H₂S into the reactor with a syringe.

The infrared absorption spectra of adsorbed H₂S and pyridine on the catalyst surface were recorded on a Hitachi infrared spectrometer model 260-10 equipped with a conventional *in situ* cell connected to a vacuum line. About 0.03g of fine powdered catalysts were formed into a thin disk of 20mm in diameter under a pressure of 300kg/cm². The disk was placed in the cell and evacuated *in situ* at 450°C for 1 or 2hr as the pretreatment. And 40torr of H₂S was introduced into the cell, which was maintained at a given temperature for 0.5hr. Then, infrared spectra of adsorbed H₂S on catalysts were observed at room temperature with or without H₂S in gas phase. The infrared spectra of H₂S in gas phase were not observed because of the narrow interval of the sample setting position of infrared cell used in this study.

For the examination of the change of acidic properties of catalysts by the adsorption of H₂S, the change of infrared spectra of pyridine adsorbed on catalysts before and after pretreatment with H₂S were observed at room temperature.

2. 2 Catalysts

Metal ion exchanged Y zeolites (MeY) were prepared from sodium Y zeolite (NaY ; SK-40) by means of ion exchange from an aqueous solution of metal ions followed by washing. The percentage of ion exchange was determined by measuring the concentration of sodium ions, which were extracted into the solution after ion exchange, by use of atomic absorption spectrometer. The results obtained are shown in Table 1. All zeolites were calcined in air at 500°C for 4hr before use.

Various metal ions were supported on silica-alumina, silica gel and alumina by the ion exchange method. These supported metal ion catalysts were prepared by soaking uncalcined silica-alumina, silica gel and alumina in an aqueous solution of metal chloride or metal nitrate for about 7 days followed by washing. Then, these catalysts were calcined in air at 500°C for 4hr before use. A part of the catalysts was dissolved in a mixed solution of hydrofluoric acid and sulfuric acid. The amount of metal ions supported on the catalyst surface were determined by measuring the concentration of metal ions in this solution by use of flame photometry and chelatometric titration. The results obtained are shown in Table 3 and 4.

2. 3 Materials

High-purity H₂S supplied by Takachiho Kagaku Kogyo Co. was used without further purification. Pyridine(GR) supplied by Nakarai Chemicals Co. was used after purification of vacuum distillation. Cumene(GR), toluene(GR), o-xylene(GR) and 2-propanol(GR) supplied by Nakarai Chemicals Co. were used without further purification, since no impurities were detected by the gaschromatographic analysis.

3. Results and Discussion

3.1 Effect of H₂S Treatment on Catalytic Activities of Various MeY Catalysts

The catalytic activities of various MeY catalysts with and without H₂S treatment for cumene cracking reaction at 300°C are shown in Table 1. The catalytic activities of NaY, CaY, BaY, MgY, MnY, FeY and CrY were scarcely changed by H₂S treatment. However, the catalytic activities of CdY, NiY, CuY, AgY, CoY and ZnY were increased from 1.3- to 5.5-fold by this treatment. A marked differences in the ratios of activity increase (k_t/k_o in Table 1) were observed between different metal ion forms.

The amount of adsorbed H₂S on MeY catalysts were also shown in Table 1. H₂S adsorbs on CdY, NiY, AgY, CuY and CoY more than 3.6×10^{-4} mol/g-cat at 300°C. However, on the other MeY catalysts, the amount of H₂S adsorbed were less than 1.0×10^{-5} mol/g-cat at 300°C. From the above results, it was found that no remarkable change in catalytic activities by H₂S treatment was observed on NaY, CaY, BaY, MgY, MnY, FeY and CrY, since H₂S scarcely adsorbs on these MeY catalysts.

The relation between the pulse number and cumene cracking activity of CdY before and after H₂S treatment are shown in Fig. 1. The reaction was carried out at 300°C. The catalytic activity of CdY before H₂S treatment was very low and scarcely changed with an increase of the pulse number. On the other hand, the catalytic activity of CdY after H₂S treatment was very high from the first pulse, then catalytic activity gradually decreased with an increase of

Table 1. Initial activities of various metal ion exchanged Y zeolite catalysts for cumene cracking at 300°C.
H₂S pretreatment temperature=300°C, Amount of H₂S injection=2ml (8.3×10^{-5} mol), Carrier gas flow rate=27ml/min, Volume of cumene pulse=2 μ l

Catalyst	%-Ion exchanged	$k_o \times 10^{-2}$ ^{a)} (ml/g·min)	$k_t \times 10^{-2}$ ^{b)} (ml/g·min)	k_t/k_o ^{c)}	$v \times 10^4$ ^{d)} (mol/g-cat)
Na Y	—	0.	0.	—	<0.1
Ca Y	73.8	5.1	5.1	1.0	<0.1
Ba Y	79.5	0.	0	—	<0.1
MgY	69.2	4.6	4.5	1.0	<0.1
MnY	69.3	4.9	5.1	1.0	<0.1
Fe Y	92.9	0.	0	—	<0.1
Cr Y	98.3	0.	0	—	<0.1
Cd Y	75.2	2.9	15.9	5.5	5.7
Cu Y	77.3	3.1	16.5	5.3	5.6
Ni Y	68.8	3.1	15.7	5.1	6.0
AgY	93.9	2.0	9.2	4.6	10.3
Co Y	71.4	5.2	12.8	2.5	3.6
Zn Y	78.6	12.9	17.1	1.3	<0.1

a) First order rate constant before pretreatment with H₂S

b) First order rate constant after pretreatment with H₂S

c) Ratio of activity increase

d) Amount of H₂S adsorbed on MeY catalysts

the pulse number. However, a decreased activity of CdY was almost regenerated by calcination in oxygen stream at 500°C for 4hr followed by the treatment with H₂S. This result indicates that the main cause of the deactivation of H₂S-treated CdY is the accumulation of carbonaceous polymer compounds on the catalyst surface.

The effect of pyridine poisoning on catalytic activity are shown in Fig. 1 (curve B). The catalytic activity of H₂S-treated CdY perfectly disappeared by the injection of pyridine, indicating that the acid sites were formed on CdY by the treatment with H₂S. Since the differences in the effect of H₂S treatment on the catalytic activity of MeY were observed between different metal ion forms, the increase in catalytic activity of MeY was attributed to the formation of acid sites in terms of adsorbed H₂S on exchangeable metal ions in MeY catalysts.

3. 2 Effect of H₂S Treatment on The Catalytic Activities of CdY for Various Acid Catalyzed Reactions

The effect of H₂S treatment on catalytic activities of CdY for various acid catalyzed reactions were examined using a continuous flow reactor. The catalytic activities of CdY without and with H₂S treatment are shown in Table 2. From this result, it was found that the catalytic activities of CdY for various acid catalyzed reactions such as the cracking of cumene, the disproportionation of toluene, the isomerization and disproportionation of o-xylene, and the dehydration of 2-propanol were increased by H₂S treatment. In all reactions, the distribution of products scarcely changed by H₂S treatment. This result indicates that the property of acid sites formed by H₂S treatment is the same as that of original acid sites on MeY catalyst

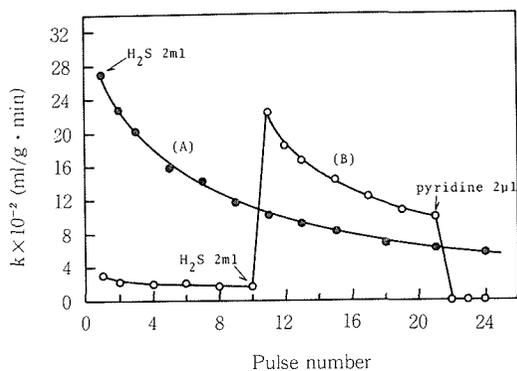


Fig. 1 Effects of H₂S injection on the course of cracking reaction and of the pyridine poisoning on the activity of CdY at 300°C

Table 2. Catalytic activities of CdY zeolite without and with H₂S pretreatment for acid catalyzed reactions

Reactant	Reaction	Reaction temperature (°C)	Feed rate (ml/min)	Weight of catalyst (mg)	Without H ₂ S		X _t /X ₀
					X ₀ (%)	X _t (%)	
Cumene	Cracking	300	4.32x10 ⁻²	500	5.95	62.2	10.4
Toluene	Disproportionation	400	4.32x10 ⁻²	500	2.47	16.4	6.6
o-Xylene	Isomerization	350	4.32x10 ⁻²	500	1.17	22.8	19.4
	Disproportionation				1.00	23.1	23.1
	Total				2.17	45.9	21.1
2-Propanol	Dehydration	150	1.37x10 ⁻³	10	39.5	47.4	1.2

The reactions were carried out using a continuous flow reactor.

X₀ and X_t; Conversion before and after pretreatment with H₂S

surface.

3.3 Infrared Spectra of H₂S Adsorbed on MeY

The infrared spectra of H₂S adsorbed on CdY, NiY, CuY, AgY, CoY and ZnY are shown in Fig. 2.¹⁰⁾ The catalytic activities of these MeY catalysts were increased by H₂S treatment as shown in Table 1. In the spectra of the background of these MeY catalysts evacuated at 450°C for 2hr, surface hydroxyl groups at around 3640 and 3550 cm⁻¹ were observed. The intensities of bands of these two hydroxyl groups on all MeY were increased by the adsorption of H₂S at temperatures ranging from room temperature to 300°C. Simultaneously, thiol groups were observed at around 2550 cm⁻¹ on all samples. These increased hydroxyl group bands disappeared by the adsorption of pyridine. And the adsorption bands of pyridinium ion at 1545cm⁻¹ on all MeY catalysts were observed. This result indicates that new hydroxyl groups formed by the adsorption of H₂S show Brönsted acidity.

On the other hand, the infrared spectra of NaY, CaY and MgY were not changed by the adsorption of H₂S at temperatures ranging from room temperature to 300°C. In the case of these MeY, an increase in intensity of hydroxyl groups and the absorption bands of thiol groups were not observed after the adsorption of H₂S.

From the above results, an increase in catalytic activity of MeY catalysts by H₂S treatment was attributed to the formation of new acidic hydroxyl groups, i. e. Brönsted acid sites in terms of adsorbed H₂S on metal ions in MeY catalysts. The mechanism of the formation of acidic hydroxyl groups on MeY zeolites by the adsorption of H₂S were proposed as below.

In this mechanism, H₂S adsorbs dissociatively on metal ions to produce Me⁺·SH and H⁺ species. This proton attaches to the oxygen anion of zeolite skeletal structure forming acidic hydroxyl groups. As the adsorption temperature of H₂S increased, the band intensities of acidic hydroxyl groups increased and the band intensities of thiol groups decreased or disappeared. This

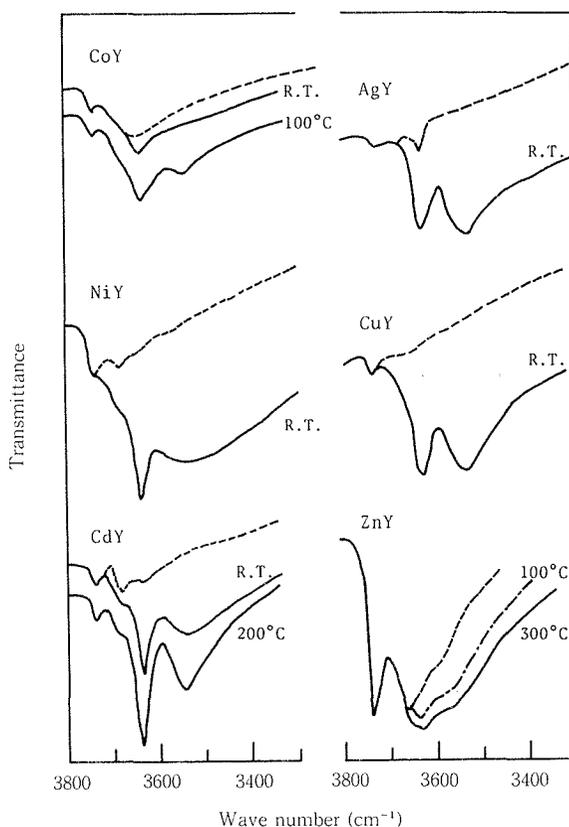
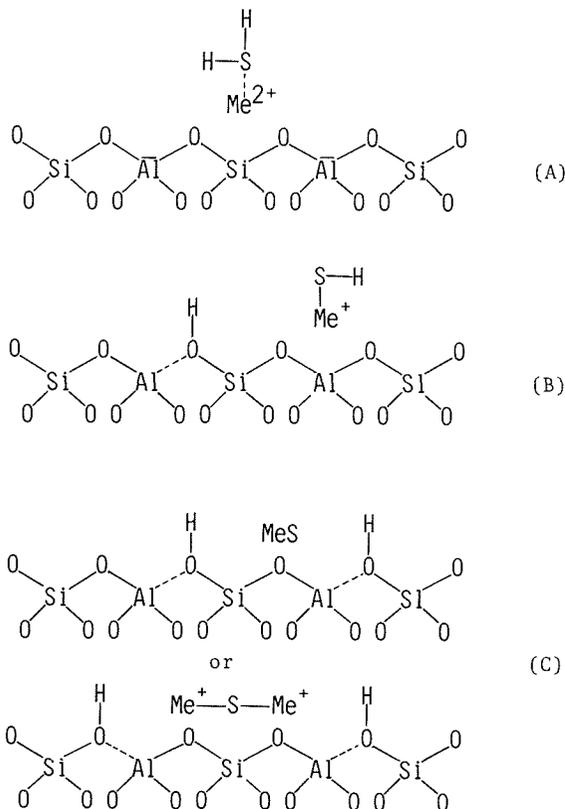


Fig. 2 Infrared spectra of hydroxyl groups on CdY, NiY, CuY, CoY, ZnY and AgY after adsorption of H₂S at various temperature. Broken line; background after evacuation at 450°C for 2hr, R. T.=Room temperature



indicates that the dissociation of H_2S proceeds with the increasing of the adsorption temperature and the thiol groups ($\text{Me}^+\text{-SH}$) disappeared with the formation of MeS or $\text{Me}^+\text{-S-Me}^+$ species.

3.4 Effect of H_2S Treatment on The Catalytic Activities of Metal Ions Supported on Silica-Alumina

From the results obtained in previous sections, it was found that H_2S adsorbs on Metal ions in zeolites to form new acid sites on MeY surface. This implies that the promotive effect of H_2S might be observed on metal ions supported on other solid catalysts.

The cumene cracking activities of various metal ions supported on silica-alumina ($\text{Me-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Me}=\text{Na}^+$, Ca^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , Cu^{2+} , Ni^{2+} , Ag^+ and Co^{2+}) without and with H_2S treatment are shown in Table 3. The cracking reaction was carried out at 350°C using a pulse reactor after the catalyst bed was treated with H_2S at 350°C and it was kept in helium stream for 1 min. The catalytic activities of $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{Na-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Ca-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Mg-SiO}_2\text{-Al}_2\text{O}_3$ and $\text{Zn-SiO}_2\text{-Al}_2\text{O}_3$ were not changed by H_2S treatment. However, the catalytic activities of $\text{Cd-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Cu-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Ni-SiO}_2\text{-Al}_2\text{O}_3$, $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$ and $\text{Co-SiO}_2\text{-Al}_2\text{O}_3$ were increased by this treatment, as well as zeolite catalysts. The increased activities by H_2S treatment were markedly decreased with increase of the pulse number.

The relation between holding time in a helium stream after H_2S treatment and catalytic

Table 3. Initial activities of metal ions supported on silica-alumina for cumene cracking at 350°C
 H₂S pretreatment temperature = 350°C, Amount of H₂S injected = 2ml, Carrier gas flow rate = 30ml/min, Volume of a cumene pulse = 2μl

	Amount of metal ion supported (mmol/g-SiO ₂ -Al ₂ O ₃)	$k_0 \times 10^{-2}$ ^{a)} (ml/g·min)	$k_1 \times 10^{-2}$ ^{b)} (ml/g·min)	k_1/k_0^c
Na-SiO ₂ -Al ₂ O ₃	1.04	0.85	0.84	1.0
Ca-SiO ₂ -Al ₂ O ₃	0.264	2.38	2.42	1.0
Mg-SiO ₂ -Al ₂ O ₃	0.300	2.48	2.50	1.0
Zn-SiO ₂ -Al ₂ O ₃	0.020	4.32	4.26	1.0
Cd-SiO ₂ -Al ₂ O ₃	0.196	3.20	4.62	1.4
Co-SiO ₂ -Al ₂ O ₃	0.317	2.61	3.58	1.4
Ni-SiO ₂ -Al ₂ O ₃	0.351	2.43	3.92	1.6
Cu-SiO ₂ -Al ₂ O ₃	0.585	0.67	9.42	14
Ag-SiO ₂ -Al ₂ O ₃	1.08	0.66	13.1	20
SiO ₂ -Al ₂ O ₃	—	4.52	4.45	1.0

a), b) and c) are same as in Table 1

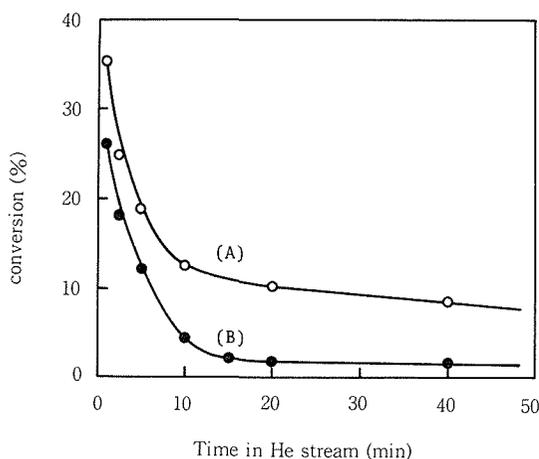


Fig. 3 Effect of time in a He stream after H₂S injection on the activities of Me-SiO₂-Al₂O₃ for cumene cracking at 350°C. These catalysts were kept in the He stream before cumene cracking

(A) : Ag-SiO₂-Al₂O₃
 (B) : Cu-SiO₂-Al₂O₃

activities are shown in Fig. 3. The catalytic activity of H₂S-treated catalysts was decreased with the increase of holding time in a helium stream. The activities of H₂S-treated MeY zeolites were not changed by the same treatment.

The infrared spectra of H₂S adsorbed on Me-SiO₂-Al₂O₃ are shown in Fig. 4. The spectra A in Fig. 4 indicates the background spectra of Me-SiO₂-Al₂O₃ after the evacuation at 450°C for 2hr. The absorption bands of hydroxyl groups at 3740cm⁻¹ were observed in spectra A. No remarkable change of bands in the hydroxyl group region on Me-SiO₂-Al₂O₃ surface were

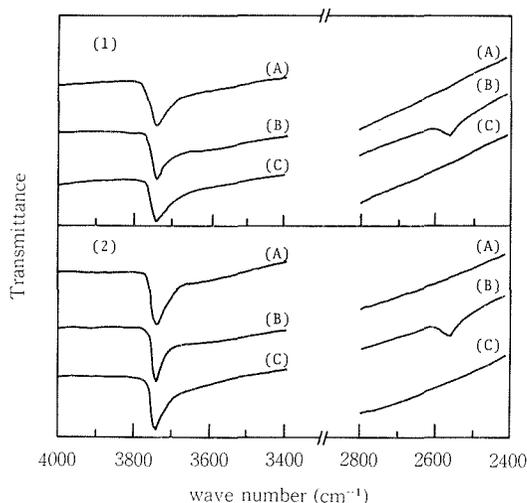


Fig. 4 Infrared spectra of H_2S adsorbed on the $\text{Me-SiO}_2\text{-Al}_2\text{O}_3$

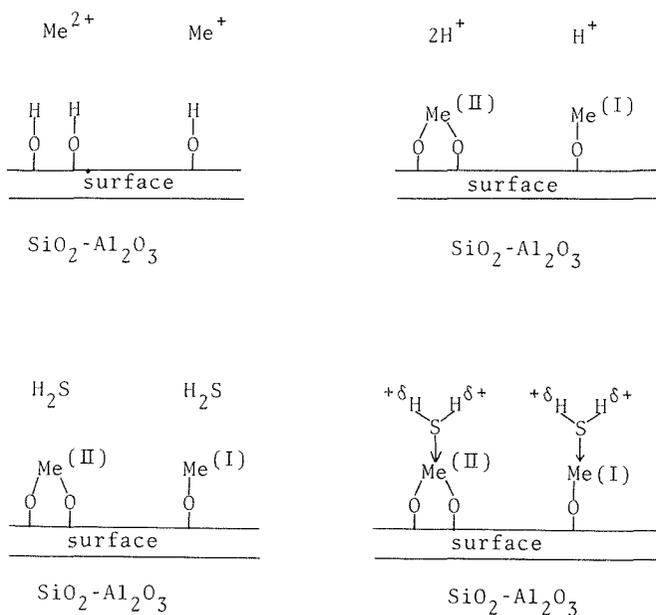
[A] : Background spectra after evacuation at 450°C for 1hr

[B] : In the presence of gaseous H_2S (40mmHg)

[C] : Evacuation at room temperature for 1hr

[1] : $\text{Cu-SiO}_2\text{-Al}_2\text{O}_3$, [2] : $\text{Ag-SiO}_2\text{-Al}_2\text{O}_3$

observed after the adsorption of H_2S at 350°C , but the thiol group of H_2S were observed at around 2560cm^{-1} in the presence of gas phase (spectra B). However, these thiol group bands disappeared by the elimination of H_2S in gas phase. Then, the spectra B was returned to its original background by this treatment as shown in spectra C. These results indicate that H_2S adsorbs on $\text{Me-SiO}_2\text{-Al}_2\text{O}_3$ surface reversibly with a weak coordination to metal ions on $\text{Me-SiO}_2\text{-Al}_2\text{O}_3$ surface as shown below ;



In this mechanism, thiol groups of H_2S weakly coordinated to metal ions act as Brønsted acid sites.

3. 5 Effect of H₂S Treatment on The Catalytic Activities of Metal Ions Supported on Silica gel and Alumina

The catalytic activities of metal ions supported on silica gel and alumina (Me-SiO₂ and Me-Al₂O₃, Me=Na⁺, Ca²⁺, Mg²⁺, Zn²⁺, Cd²⁺, Cu²⁺, Ag⁺, Co²⁺ and Ni²⁺) without and with H₂S treatment for the dehydration of 2-propanol at 200°C are shown in Table 4. The catalytic activities of Ag-SiO₂, Cu-SiO₂, Cd-SiO₂, Ni-SiO₂, Co-SiO₂, Ag-Al₂O₃, Cu-Al₂O₃, Cd-Al₂O₃, and Co-Al₂O₃ were increased by H₂S treatment. The catalytic activities of the other Me-SiO₂ and Me-Al₂O₃ are not changed by this treatment. Propylene and water were mainly produced as products of inner-molecular dehydration. A trace amount of products of intramolecular dehydration and dehydrogenation were formed. No remarkable change of the distribution of reaction products were observed by H₂S treatment. H₂S adsorbed on Me-SiO₂ and Me-Al₂O₃ were not easily desorbed by holding in a helium stream. This result agreed with that obtained

Table 4. Initial activities of metal ions supported on silica gel and alumina for dehydration of 2-propanol at 200°C
H₂S pretreatment temperature=200°C, Amount of H₂S injected=2ml, Carrier gas flow rate=30ml/min, Volume of a 2-propanol pulse=2μl

	Amount of metal ion supported (mmol/g-cat)x10 ²	X ₀ (%)	X ₁ (%)	X ₁ /X ₀ ^{a)}
Ag · SiO ₂	0.810	8.93	37.4	4.19
Cu · SiO ₂	0.749	4.01	30.4	7.58
Cd · SiO ₂	1.20	10.1	22.7	2.24
Ni · SiO ₂	1.12	16.0	25.4	1.59
Co · SiO ₂	0.921	15.4	21.5	1.39
Zn · SiO ₂	0.298	10.9	11.4	1.05
Ca · SiO ₂	0.392	6.85	7.14	1.04
Mg · SiO ₂	1.52	15.9	15.8	0.99
Na · SiO ₂	2.08	0	0	—
SiO ₂	—	11.9	12.2	1.03
Ag · Al ₂ O ₃	4.36	11.6	18.2	1.57
Cu · Al ₂ O ₃	13.5	7.59	15.8	2.08
Cd · Al ₂ O ₃	16.1	11.3	14.4	1.28
Co · Al ₂ O ₃	15.4	10.8	12.4	1.14
Ni · Al ₂ O ₃	34.6	12.7	11.9	0.94
Zn · Al ₂ O ₃	2.01	17.2	17.5	1.02
Ca · Al ₂ O ₃	0.92	13.0	12.6	0.96
Mg · Al ₂ O ₃	27.4	10.4	10.9	1.05
Na · Al ₂ O ₃	3.35	7.38	7.48	1.01
Al ₂ O ₃	—	7.80	8.04	1.03

a) X₀, X₁: Conversion without and with H₂S pretreatment

Table 5. Promotive effect of H₂S on the catalytic activities of metal ions supported on various solid catalysts for the acid catalyzed reactions

	Cd ²⁺	Ag ⁺	Cu ²⁺	Co ²⁺	Ni ²⁺	Zn ²⁺	Ca ²⁺	Mg ²⁺	Na ⁺	Ba ²⁺	Mn ²⁺	Fe ³⁺	Cr ³⁺
HSAB ^{a)}	S	S	M	M	M	M	H	H	H	H	H	H	H
Y-zeolite	o	o	o	o	o	o	x	x	x	x	x	x	x
SiO ₂ -Al ₂ O ₃	o	o	o	o	o	x	x	x	x				
SiO ₂	o	o	o	o	o	x	x	x	x				
Al ₂ O ₃	o	o	o	o	x	x	x	x	x				

a) Hard and soft acids and bases; S: soft acid, H: hard acid, M: medium acid o: Promoted
x: No-effect

in the case of zeolite catalysts. Therefore, H₂S adsorbs dissociatively on metal ions in Me-SiO₂ and Me-Al₂O₃ to form the acid sites the same as that on MeY zeolites.

3. 6 Affinity of Metal Ions toward H₂S

The promotive effect of H₂S on the catalytic activities of metal ions supported on Y-zeolites, silica-alumina, silica gel and alumina catalysts are summarized in Table 5. It was found that the activities of catalysts containing the same kinds of metal ions were promoted by H₂S treatment. Hence, the affinity of metal ions toward H₂S were examined. HSAB in Table 5 indicate the classification based on the concept of hard and soft bases and acids that was first proposed by R. G. Pearson¹¹⁾. The symbol H, S and M in Table 5 indicate the hard acids, soft acids and medium acids, respectively. From this concept, it was proposed that hard acids bind strongly to hard bases and soft acids bind strongly to soft bases. H₂S was classified as a soft base. Hence, H₂S binds strongly to metal ions classified as soft acids. From the results in Table 5, all of the catalysts increased in activities by H₂S treatment contain the soft or medium acids. Hence, it was concluded that an increase in catalytic activity was strongly dependent on the affinity of metal ions in catalysts toward H₂S.

4. Conclusion

For acid catalyzed reactions, the catalytic activities of metal ion exchanged Y zeolites, MeY (Me=Cd²⁺, Cu²⁺, Ni²⁺, Co²⁺, Ag⁺, and Zn²⁺), were enhanced by the treatment with H₂S. The infrared spectra of MeY catalysts treated with H₂S indicated the formation of new hydroxyl groups on the surface. An increase in Brønsted acidity of MeY was also observed after the pretreatment with H₂S in the infrared spectra of chemisorbed pyridine on MeY. Thus, it was concluded that an increase in catalytic activity of MeY by the treatment with H₂S attributed to the formation of new acidic hydroxyl groups, i. e., Brønsted acid sites, in terms of irreversibly adsorbed H₂S on Metal ions in MeY zeolites.

The catalytic activities of various metal ions supported on silica-alumina, silica gel and alumina (Me-SiO₂-Al₂O₃, Me-SiO₂ and Me-Al₂O₃ Me=Ag⁺, Cu²⁺, Cd²⁺, Co²⁺ and Ni²⁺) for acid catalyzed reactions were also enhanced by the treatment with H₂S. The infrared spectra of the Me-SiO₂-Al₂O₃ catalyst treated with H₂S indicated the formation of weak bonding between H₂S and metal ions supported on Me-SiO₂-Al₂O₃. These data strongly suggested that an in-

crease in catalytic activity of Me-SiO₂-Al₂O₃ by the treatment with H₂S was attributed to reversibly adsorbed H₂S molecules acting as Brönsted acid sites on metal ions supported on silica-alumina. For Me-SiO₂ and Me-Al₂O₃ catalysts, it was considered that an increase in the catalytic activities by the treatment with H₂S attributed to the formation of new acid sites formed by H₂S irreversibly adsorbed on metal ions supported on SiO₂ and Al₂O₃.

From the concept of hard and soft bases and acids, it was found that H₂S binds strongly to Cd²⁺, Ag⁺, Cu²⁺, Co²⁺ and Ni²⁺ ions. Thus, it was concluded that an increase in activity was strongly dependent on the affinity of metal ions in catalysts toward H₂S.

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